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ScienceDirect

Energy Procedia 89 (2016) 323 – 327

Energy Procedia

CoE on Sustainable Energy System (Thai-Japan), Faculty of Engineering, Rajamangala University of Technology Thanyaburi (RMUTT), Thailand

Role of crystallinity on moisture absorption and mechanical performance of recycled PET compounds

Takanori Negoro[a,b], Wiranphat Thodsaratpreeyakul[a], Yoko Takada[b], Supaphorn Thumsorn[a] *, Hiroyuki Inoya[a] and Hiroyuki Hamada[a]

[a] *Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto, 606-8585, Japan*
[b] *Thai Negoro Co., Ltd., Bangpoo Industrila Estate, Samutprakarn, Thailand*

Abstract

Recycle poly(ethylene terphthalate) (RPET) was compounded with talc, glass bead and PEG in twin screw extruder with different cooling systems of hot air cooling and water cooling processes. The air cooling system allowed slow cooling and higher crystallized of RPET in the compounds, which resulting in higher crystllinity in the compounds as compared to the water cooling. Moisture content of the compounds decreased when increasing crystallinity. It is interesting to note that tensile properties of the RPET compunds would enhance when incorporated with talc filler and when lower moisture content values in the RPET compounds.

Peer-review under responsibility of the organizing committee of the 12th EMSES 2015

Keywords: crystallinity; filler; moisture; recycled PET

1. Introduction

Poly(ethylene terephthalate) (PET) is an engineering thermoplastic. It has been known as hygroscopic material, which is generally easily absorb moisture and water in the surrounding environment. Higher and excess of moisture content in the materials influence on the declination of physical and mechanical properties of the final products,

* Corresponding author. Tel.: +81 75-724-7844; fax: +81 75-724-7844.
E-mail address: nooh17@gmail.com

Peer-review under responsibility of the organizing committee of the 12th EMSES 2015
doi:10.1016/j.egypro.2016.05.042

especially when using recycled PET (RPET). From the literatures, PET at the crystalline stage has been lower moisture content as compared to the amorphous one [1-2]. Therefore, RPET would be less moisture content when enhancing its crystalline stage.

Hosseini et al. [3] reported that hydrolytic degradation of PET was affected by water content and carboxyl end group in polyester-chain. A strong hydrolytic degradation was induced at humidity condition and high temperature. In addition, pellets geometries i.e. size and shape are influenced on moisture absorption of polymers [2, 4]. Thumsorn et al. [4] showed that finer geometries, such as powders of RPET and recycled polypropylene (RPP) blends, were found to have higher moisture absorption rates due to their large surface area although they could be easily dried.

The incorporation of fillers in polymer is considering on the reduction of the water uptake and the moisture absorption of polymers [5-7]. Thumsorn et al. [5] revealed that moisture contents of RPET and RPP blends decreased with adding $CaCO_3$. Balakrishna et al. [6] reported that the water uptake of the hybrid composites was reduced with higher talc filler loading due to the hydrophobicity of talc. In addition, talc has been used for enhanced crystallinity of polymer, which could enhance thermal and mechanical properties of PET and RPET [8-10]. Su et al. [11] used expanded graphite and poly(ethylene glycol) (PEG) for enhanced crystallization behavior of PET. From this research, expanded graphite acted as a nucleating agent, while PEG was a plasticizer to improve mobility of PET chains. The adding of expanded graphite and PEG resulted in fast crystallization kinetic in non-isothermal crystallization.

This research focused on improving crystallinity of RPET by incorporation with additives of talc, glass bead and PEG. The air cooling process was used for enhancing crystallization process of RPET during compounding. The effects of additives and cooling processes on physical and mechanical properties of RPET compound were investigated in this study.

2. Experimental

2.1. Materials

RPET was supplied by Negoro Sangyo Co., Ltd., Japan (IV = 0.65 dl/g). Fine talc powder (Nano ACE series D-1000) with an average particle size of 1 μm was provided from Nippon Talc Co., Ltd, Japan. Spherical micro glass bead (EMB-10) with an average particle size of 5 μm was kindly supplied by Plotters-Ballotini Co., Ltd, Japan. Talc and Glass bead contents were used at 3 wt%. Poly(ethylene glycol) (PEG6000) was supplied from EMD Millipore Corporation, USA. PEG was used at 3 wt%. The specimens are referred as T, PT, G and PG, which represented for RPET filled with talc, PEG with talc, glass bead and PEG with glass bead, respectively.

Table 1. Composition and sample designation.

Samples	RPET (wt%)	Filler content (wt%)		
		Talc	Glass bead	PEG
RPET	100	0	0	0
T5	95	5	0	0
PT5	92	5	0	3
G5	95	0	5	0
PG5	92	0	5	3

2.2. Sample preparation

RPET fillers and PEG were compounded in a twin-screw extruder. The barrel temperature was set at 255-285 °C with screw speed of 100 rpm. Extruded strands were dried along the conveyer using two systems by hot air cooling controlled at 140 °C, which is referred as A and water cooling, which is referred as W before pelletizing. RPET compound pellets were kept in aluminum bags before measuring moisture contents. RPET compound were dried at 115 °C for at least 8 h before injection molded to dumbbell specimens.

2.3. Characterization

Differential scanning calorimetry (DSC2920, TA Instruments, USA) was used for characterized thermal properties and crystallinity of the compounds. The compounds of 5 mg were cut from the pellets and placed in an aluminum pan. Temperature was set from 30-300 °C at heating rate of 10 °C/min under nitrogen atmosphere. The crystallinity of polymer was calculated from the following equation.

$$\%X_c = \frac{(\Delta H_m - \Delta H_{cc}) \times 100}{\Delta H_{f100}} \times \frac{1}{W_p} \quad (1)$$

Where
X_c = Degree of crystallinity
W_p = Weight fraction of polymer
ΔH_m = Enthalpy of melting enthalpy
ΔH_{cc} = Enthalpy of cold crystallization enthalpy
ΔH_{f100} = Heat of fusion of 100% PET Crystallization = 140 J/g [10]

Moisture content of the compounds was analyzed by Karl Fischer titration (MKC-610, Kyoto Electrics Manufacturing, Co., Ltd., Japan) at temperature of 25 °C and relative humidity of 60%. Both as-received RPET and RPET compounds were conditioned in the testing room before measuring the moisture content.

Mechanical properties were carried out on tensile testing and flexural testing using an Instron universal testing machine (Instron4206, USA). The tensile test was done according to ASTM D-638 at cross head speed of 20 mm/min.

3. Results and Discussion

3.1. Thermal properties and crystallinity of RPET compounds

Fig. 1 shows DSC thermograms of RPET compounds with different in extruder cooling processes. It can be seen only melting endotherms of RPET compounds using air cooling, which presented melting temperatures of RPET in the RPET compounds as presented in Fig. 1 (a). On the other hand, it can be observed endothermic steps of glass transition temperatures, exothermic curves of cold crystallization temperatures and melting endotherm of melting temperatures of RPET in the RPET compounds as shown in Fig. 1 (b). It was considered that RPET was slow cooling and PET was possible more crystallized during hot air cooling than in the compounds using water cooling system. From Table 2, crystallinity values of the compounds using air cooling were about 30-33 %, which were over 50% higher than the compounds by the water cooling one. Therefore, the air cooling process provided better crystallinity of the RPET compounds.

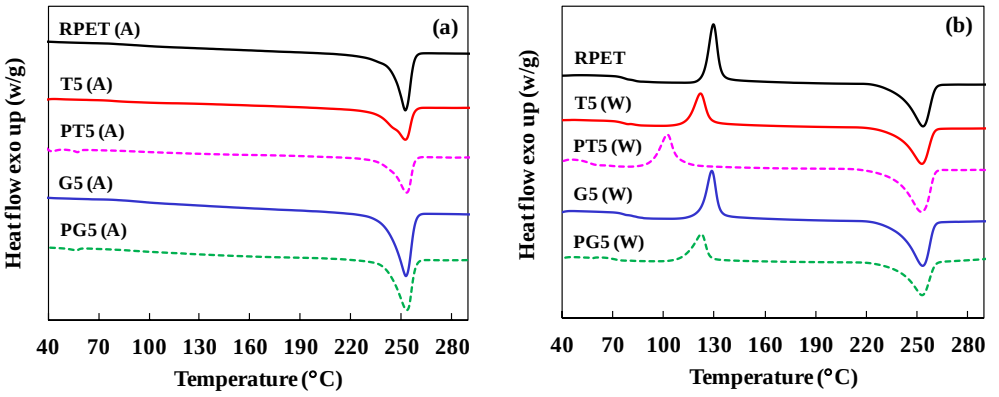

Fig. 1. DSC thermograms of RPET compounds (a) air cooling (b) water cooling.

Table 2. Crystallinity of RPET compounds after exposure at 3 and 50 days.

Samples	Crystallinity (%)			
	Air cooling		Water cooling	
	3 days	50 days	3 days	50 days
RPET	32.9	31.7	8.9	9.9
T5	31.4	32.7	12.7	12.7
PT5	29.5	29.8	17.1	13.9
G5	31.3	30.8	14.0	11.7
PG5	29.7	26.1	17.7	17.2

Table 3 tabulates moisture content of RPET compounds after exposure for 3 and 50 days. Moisture content of the compounds increased with increasing the exposure times due to hygroscopic of PET. It can be note that moisture content of the RPET compounds with adding of talc and glass bead was lower than neat RPET. It was considered that filler enhanced crystallinity of the compound, which would result in lower moisture absoprtion of the materials. Fig. 2 illustrates the relationship between moisture absorption and crystallinity of RPET compounds by air and water cooling system after exposured in aluminum bags for 3 days. From the results, the RPET compounds were lower moisture absorptions at higher crystallinity. It was corresponding that moisture absorption is depended upon the crystallinity of the resin. Hence, moisture content of the resin decreased with increasing crystallinity in the compounds, which would yield better in mechanical properties of the RPET compounds.

Table 3. Moisture content of RPET compounds after exposure at 3 and 50 days.

Samples	Moisture content (%)			
	Air cooling		Water cooling	
	3 days	50 days	3 days	50 days
RPET	0.009	0.050	0.085	0.188
T5	0.007	0.030	0.112	0.172
PT5	0.012	0.061	0.562	0.932
G5	0.004	0.049	0.029	0.047
PG5	0.018	0.058	0.030	0.049

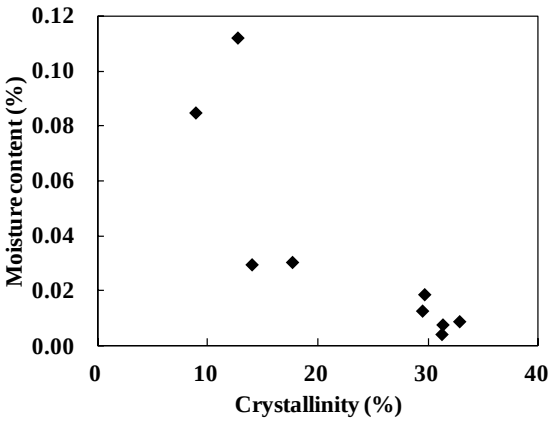

Fig. 2. Relationship between crystallinity and moisture content of RPET compounds

3.2. Tensile properties of injection molded RPET compounds

Tensile properties of the RPET compounds by air cooling and water cooling processes are presented in Fig.3. Tensile modulus and tensile strength of the RPET compounds increased when adding with talc filler as shown in Fig. 3 (a) and Fig. 3 (b), respectively. From the results, tensile modulus of the talc filled RPET compounds by the water cooling was higher than air cooling system, which might be due to large amorphous fraction in these compounds. On the other hand, tensile strength of the RPET compounds was almost unchanged when using the air cooling or the water cooling processes.

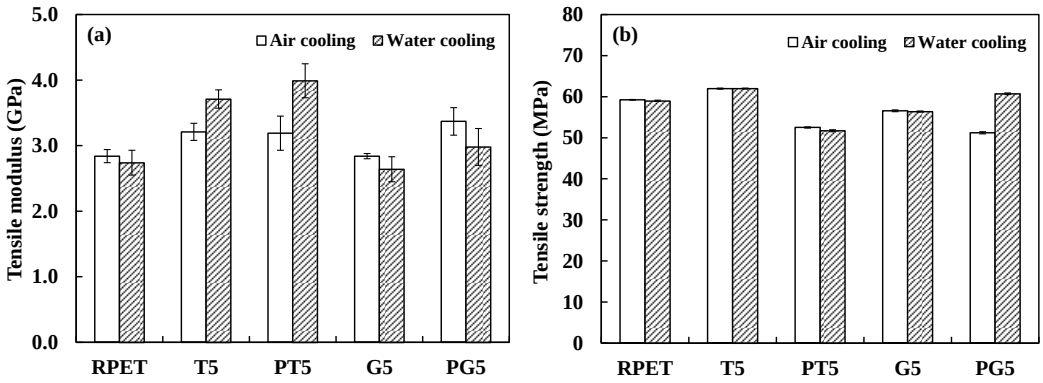

Fig. 3. Mechanical properties of injection molded RPET compounds (a) Tensile modulus (b) Tensile strength.

4. Conclusions

The air cooling process obtained higher crystallinity of the RPET compounds, which resulting in lower moisture contents in these compounds. However, moisture content values of the compounds by the air cooling system were still high and were recommended to dry before fabrication to products in order to yield superior mechanical properties of the RPET compounds products.

References

[1] PET Business Group, Drying RELPET, Reliance Industries Limited; 2003.
[2] Scheirs J, Long TE, edited, Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters, John Wiley & Sons; 2003. p. 495.
[3] Hosseini SS, Taheri S, Zadhoush A, Mehrabani-Zeinabad A, Hydrolytic degradation of poly(ethylene terephthalate), J Appl Polym Sci 2007;103: 2304-2309.
[4] Thumsorn S, Yamada K, Leong YW, Hamada H, Effect of pellet size and compatibilization on thermal decomposition kinetic of recycled polyethylene terephthalate/recycled polypropylene blend, J Appl Polym Sci 2012;124:1605-1613.
[5] Thumsorn S, Yamada K, Leong YW, Hamada H, Thermal decomposition kinetic and flame retardancy of $CaCO_3$ filled recycled polyethylene terephthalate/recycled polypropylene blend, J Appl Polym Sci 2013;127:1245-1256.
[6] Balakrishna NS, Ismali H, Othman N, Processing, Mechanical, and Thermal Properties of Polypropylene/Rattan Powder/Talc Hybrid Composites, BioResources 2013;8,:6409-6413.
[7] Weibeck H, Borrelly DF, Xavier C, Santos PS, Asciutti SA, Corrêa MP, The effect of silane coupling agents on a composite polyamide-6/talc, Braz J Chem Eng 1998;15:406-409.
[8] Jiang XL, Luo SJ, Sun K, Chen XD, Effect of nucleating agents on crystallization kinetics of PET, eXpress Polym Lett 2007;1:245-251.
[9] Yamada K, Thumsorn S, Effectiveness of talc filler on thermal resistance of recycled PET blends, Mater Sci Appl 2013;3:327 -331.
[10] Di Lorenzo ML, Errico ME, Avella M, Thermal and morphological characterization of poly(ethylene terephthalate)/calcium carbonate nanocomposites, J Mater Sci 2002;37:2351-2358.
[11] Su J, Yang G, Zhou T, Gao X, Wang K, Fu Q, Enhanced crystallization behaviors of poly(ethylene terephthalate) via adding expanded graphite and poly(ethylene glycol), Colloid Polym Sci 2013;291:911-917.